Lumping Nonlinear Kinetics

Lumping of the kinetics of mixtures described by a continuous distribution function of concentration is discussed for the case where individual reactions have nonlinear kinetics. The assumption of independent kinetics, which leads to a paradox, is not used. Functional-differential equations govern the kinetic behavior of the mixture. Formal solutions are presented for a class of kinetic behavior that includes Langmuir isotherm catalysis and for the special case of bimolecular reactions. A class is defined for which the kinetic functionals can be expanded in a series of integrals for which the kernels are entirely determined. Finally, a thermodynamic analysis is presented to show that the commonly accepted equilibrium theory implies a kinetic approximation of maximal rank for the kinetics at the equilibrium point.

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Introduction

The problem of lumping the kinetic behavior of mixtures of many components is an important one, since often it is impossible, or at least not easily feasible, to describe in detail the kinetic behavior of each individual component, and one is really interested only in some lumped quantity easily accessible to measurement, such as the total concentration of a whole class of components.

The literature on lumping of kinetics is abundant, and it has been reviewed by Weekman (1979) and more recently by Bischoff and Coxson (1987). Most of the published literature has to do with the case where all individual components exhibit linear (first-order) kinetics. This is certainly a very special case, and the lumping of nonlinear kinetics is of interest. Two papers in the literature which deal with nonlinear kinetics (Li, 1984; Luss and Hutchinson, 1971) use a discrete description of the composition of the mixture, i.e., one where the mixture is regarded as containing a possibly large but finite number N of components. In contrast with this, linear kinetics have often been analyzed by using a continuous description, one where the mixture is characterized by a concentration distribution function, which can easily accommodate an infinite number of reactants. The idea of describing a mixture as a continuum goes back to DeDonder (1931); it was originally discussed in terms of chemical reactions by Aris and Gavalas (1966), and a special form was applied to cracking by Aris (1968). Even if the (many) components of a mixture are known, it may be desirable to describe it as a continuous one, since then a search of the appropriate quadrature points of the resulting integrals provides a rational way of substituting a few pseudocomponents for the real ones (Shibata et al., 1987).

Since a discrete description is only a special case of a continuous one (the distribution function being the sum of a finite number of terms, each one of which is proportional to a Dirac delta function), it is hard to see why a continuous lumping of nonlinear kinetics should not be feasible. However, an attempt at doing so has been presented only recently, by Ho and Aris (1987), who point out that a straightforward extension of the linear procedure leads to what may be called the single component identity (SCI) paradox.

In this paper we present some basic ideas about the procedure for lumping nonlinear kinetics in a continuous description, and we solve the SCI paradox by showing that it is a consequence of the unwarranted assumption that the kinetics of the individual reactions in a mixture are independent of one another. In the development of the procedure we limit attention to a generalization of Langmuir isotherm kinetics (LIK), and to a class of bimolecular reactions; we also discuss the thermodynamics of continuous mixtures insofar as it reflects on their kinetic behavior.

Parameters of Nonlinear Kinetics

In the description of the composition of a mixture, individual components need to be identified, and this can be accomplished by establishing some way of labeling components. In discrete descriptions the label is simply some index $I = 1, \ldots, N$. Labels could also be chosen as some measurable quantity, such as a boiling point or carbon number, and this has been done in the literature (Bailey, 1972). In continuous descriptions, the label is

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regarded as a continuous variable, taking values over some range (typically nonnegative scalars). In the case of linear kinetics, the kinetic behavior of each species is entirely characterized by the value of the kinetic constant k, and hence k itself may be used as a label. The situation, however, is significantly more complex in the case of nonlinear kinetics.

We begin by considering a single-reactant isothermal system. Let $c(t)$ be the time-dependent concentration of the reactant. The kinetic equation is:

$$-dc/dt = r(c) \tag{1}$$

The operator $r(\,)$ is dimensional, in the sense that, since both the argument and the value are dimensional, the mathematical form of the $r(\,)$ operator will in general depend on the units chosen. It is always possible to transform Eq. 1 in such a way as to contain a dimensionless operator $r'(\,)$, by introducing two dimensional parameters, k and K, with units of a frequency and of an inverse concentration, respectively. Correspondingly, the dimensionless time and concentration are:

$$t' = kt \tag{2}$$

$$c' = Kc \tag{3}$$

and Eq. 1 can be recast in the following form:

$$-dc'/dt' = r'(c') \tag{4}$$

where $r'(\,)$ is now of course dimensionless.

Thus one concludes that, for general nonlinear kinetics, at least two dimensional parameters are needed. The choice of their values is arbitrary, but it can be effected in such a way as to attribute physical meaning to them. K can be so chosen that the initial value of c' is unity, and k can then be chosen in such a way that $r'(1) = 1$. In this way, $1/k$ is recognized as the intrinsic time scale of the reaction at the initial level of concentration (Astarita, 1987). While this is often useful when dealing with mixtures of at most a few components, it serves no particular purpose in the case of a mixture described by a continuous distribution function, since in such a mixture the initial concentrations of individual components may well be vanishingly small. An alternate normalization that is useful in the case of mixtures will be discussed later.

In addition to the dimensional parameters k and K, function $r(\,)$ may well contain several dimensionless parameters β_J, $J = 1, \ldots, M$. It is therefore useful to define an $(M + 2)$-dimensional vector $\boldsymbol{P}$ of kinetic parameters:

$$\boldsymbol{P} = k, K, \beta_J, \ldots, \beta_M = k, K, \beta \tag{5}$$

which characterizes the kinetic behavior of any given reactant.

One may now address the question of the continuous description of a reacting mixture. In the case of linear kinetics, each component is identified by the value of the kinetic constant k, which can thus be used as a label, and a distribution function $g(k)$ can be defined such that $g(k)dk$ is the concentration of species with kinetic constants between k and $k + dk$. Although in the general case one can still identify a parameter k having units of a frequency, this cannot be used as a label, since two species characterized by the same value of k may well have different values of K and β. It is therefore useful to introduce some independent label x, with values ranging over some interval of the positive axis (possibly from 0 to ∞), such that any given value of x identifies one particular species. The latter requirement is satisfied provided $\boldsymbol{P}$ is a unique function of x, $\boldsymbol{P} = \boldsymbol{P}(x)$. A distribution function $g(x)$ is thus introduced, and the total concentration of all reactants at time t, $C(t)$, is given by:

$$C(t) = \int g(x, t)\, dx \tag{6}$$

An important point to be made at this stage is that, of all possible nonlinear kinetics, the n-order type is dimensionally peculiar. Indeed, suppose that the reaction considered has n-order kinetics, say:

$$r(c) = bc^n \tag{7}$$

where b is (perhaps inappropriately) often called a kinetic constant. Quite obviously, Eq. 5 contains only one dimensional parameter, not two. It is easy to prove (Astarita, 1985) that the power-law form of the kinetic equation is the only nonlinear form that results in only one dimensional parameter. Notice that, of course, the linear case is a special case of the power law.

For the power-law case, vector $\boldsymbol{P}$ is two-dimensional, $\boldsymbol{P} = b, n$, with the order of reaction, n, being a β-type parameter. The Luss and Hutchinson (1971) nonlinear lumping analysis is restricted to the power-law form, and the additional hypothesis is made that the value of n is the same for all reactants in the mixture, so that each individual reactant is labeled by the value of b, not by the value of the label x. This is by no means generally possible; in fact it is a rather exceptional case, as the following two examples clearly show.

First consider the classical case of a Langmuir isotherm dominated kinetics (LIK), where Eq. 1 takes the following form:

$$-dc/dt = kc/(1 + Kc) \tag{8}$$

LIK data, if plotted on log-log coordinates, may well be represented (at least over a limited range of c values) by a power law with $0 \leq n \leq 1$. However, in actual fact the appropriate kinetic vector is $\boldsymbol{P} = k, K$, and in a mixture there is no reason to expect that the sorbability K has the same value for all components. Moreover, the apparent value of n extracted from data on a single reactant depends on the level of concentration and on the values of k and K, and is thus not expected to be the same for all reactants in the mixture.

Next consider the case of an irreversible dimerization reaction, where Eq. 1 takes the form:

$$-dc/dt = bc^2 \tag{9}$$

This is indeed in power-law form. However, a different kind of problem arises now: in a mixture of many components which may all undergo dimerization reactions, it does not make sense to suppose that each reactant is so choosy as to be able to dimerize only with another of its own kind. This means that one has to move to an analysis of the type presented by Li (1984), where the kinetic behavior of the mixture depends on parameters (such as the kinetic constant of the synthesis of two different monomers) that cannot be measured in experiments made under conditions where there is only one reactant present.

The SCI Paradox

In the case of linear kinetics, each component is labeled simply by the value of the kinetic constant k. The concentration vs. time curve for the case where there is only one reactant present is simply:

$$c(t) = c(0) \exp(-kt) \tag{10}$$

and the distribution function is $g(k, t)$, so that, for a mixture:

$$C(t) = \int g(k, t)\, dk \tag{11}$$

The Aris (1968) result is as follows:

$$C(t) = \int g(k, 0) \exp(-kt)\, dk \tag{12}$$

i.e., it is the Laplace transform of the initial distribution. The transform parameter is time itself, and the kernel of the transform, e^{-kt}, is the value of $c(t)/c(0)$ for the single-reactant case.

Ho and Aris (1987) point out that one could be tempted to extend this result to the nonlinear case by first establishing the $c(t)$ function for the single-reactant problem, say in the present terminology:

$$c(t) = F(\mathbf{P}, c(0), t) \tag{13}$$

where the analytical form of the $F(\ )$ function is of course determined by that of the $r(\ )$ function, and then use this as the basis of an alternate (nonlinear) transform of the initial distribution, say:

$$C(t) = \int F(\mathbf{P}(x), g(x, 0), t)\, dx \tag{14}$$

Equation 14 defines a nonlinear transform that properly degenerates into the Laplace transform for linear kinetics. This procedure, however, is unacceptable, for two reasons. The first is that it would only be correct if the kinetic equation for every reactant in the mixture could be written as:

$$\partial g/\partial t = -r(g) \tag{15}$$

This however is not correct, since g is not the concentration of the reactant, gdx is. Thus one should write:

$$\partial(gdx)/\partial t = -r(gdx) \tag{16}$$

and of course the dx cancels out only in the case of linear kinetics.

The other difficulty that Ho and Aris point out is that Eq. 14 does not satisfy what they call the single component identity (SCI) requirement. Stated in simple words, the SCI is the requirement that, if all components have the same values of the kinetic parameters, the lumped and unlumped descriptions have to coincide with each other—a requirement so obvious in its physical significance that any analysis which fails to satisfy it is obviously unacceptable. In order to convince oneself of the significance of the SCI requirement, consider the case of a single reactant that is however the raceme of two optical isomers. One would of course expect—if one is foolish enough to describe the kinetics by keeping track separately of the two isomers—that the result should be exactly the same as if one chose to describe the system in the natural way, since the two isomers are kinetically undistinguishable.

The mathematical formulation of the SCI requirement given by Ho and Aris is, when expressed in the present terminology:

$$\int F(\mathbf{P}(x), C(0)\delta(x - x^*), t)\, dx = F(\mathbf{P}(x^*), C(0), t) \tag{17}$$

which of course can be satisfied only if $F(\ )$ is linear in its second argument, i.e., essentially only for linear kinetics. The initial distribution considered in the lefthand side of Eq. 17 is the one corresponding to the case where all the reactants have the same value of $\mathbf{P}$, say $\mathbf{P}^*$, i.e., they are kinetically undistinguishable. It is interesting to observe that the Luss and Hutchinson (1971) analysis does not satisfy the SCI requirement. Even more convincingly, the lefthand side of Eq. 17 is not even defined unless $F(\ )$ is linear in its second argument, since the delta function is integrable only in its linear form.

The SCI requirement deserves some careful scrutiny, since the conclusion that it can only be satisfied for linear kinetics leaves one at a loss about what could be done for the lumping of many reactions characterized by nonlinear kinetics, which is certainly a conceivable possibility. As long as there is only one reactant, the kinetic equation is Eq. 1. Now consider the case of a mixture, and let c_I represent the concentration of the Ith reactant, with C being the total concentration:

$$C = \Sigma c_I \tag{18}$$

Furthermore, let $\mathbf{c}$ be the N-dimensional vector the components of which are the c_I's. The question that arises is: what is the kinetic equation for reactant I in the mixture, and the most general case possible is the one where the rate of consumption of component I is given by some function $r_I(\mathbf{c})$. One possible assumption, which results in a very significant simplification, is that of "independent" kinetics, i.e., that the rate at which reactant I is consumed depends only on the concentration c_I, say:

$$-dc_I/dt = r_I(c_I) \tag{19}$$

Although the assumption of independent kinetics is a somewhat natural one, and it does result in a very considerable simplification of the problem, it will be seen in the following that it is in fact extremely restrictive in the case of nonlinear kinetics. The Luss and Hutchinson (1971) analysis is based on the assumption of independent kinetics, while the Li (1984) analysis is not. It is interesting to observe that the fundamental analysis of lumping of linear kinetics (Wei and Kuo, 1969; Kuo and Wei, 1969) is not based on an assumption of independent kinetics. Indeed, the fundamental paper of Wei and Prater (1962), which is perhaps the oldest rigorous analysis of mixtures where many reactions with linear kinetics occur simultaneously, deals explicitly with the problem of substituting for the real components, which undergo nonindependent kinetics, a set of pseudocomponents for which the kinetics are independent.

Now suppose that the mixture is made up of different reactants which, however, all have the same kinetic equation, say:

$$r_1(\ ) = r_2(\ ) = \ldots = r_N(\ ) = r(\ ) \tag{20}$$

The rate of change of the overall concentration C is now given by:

$$-dC/dt = \Sigma r_I(c_I) = \Sigma r(c_I) \quad (21)$$

The SCI requirement for this case, however, is obviously that one should have:

$$-dC/dt = r(C) = r(\Sigma c_I) \quad (22)$$

and this is satisfied only in the special case where the $r(\,)$ operator is linear. One thus immediately obtains the following conclusion: In the case of independent kinetics, the SCI requirement can be satisfied only for linear kinetics, which is of course the essence of the Ho and Aris (1987) conclusion.

Although the discussion above has been presented for the discrete description case, it also applies to the continuous description case. Indeed, let the kinetic equation in the continuous mixture be:

$$-\partial g/\partial t = v[g(x);x] \quad (23)$$

where $v[\,]$ is a function of the value of g which also depends parametrically on x. If the kinetics are independent, there cannot of course be any parameters other than the values of $\boldsymbol{P}$, and hence Eq. 23 is the most general possible formulation of independent kinetics. Notice however that the converse is not true: as will be seen in the next section, a mixture's behavior may be entirely described by the values of $\boldsymbol{P}$, and yet the kinetics may well not be independent. Equation 23 yields:

$$-dC/dt = \int v[g(x);\,x]\,dx \quad (24)$$

Now suppose that all reactants in the mixture have the same value of $\boldsymbol{P}$, say $\boldsymbol{P}(x^*)$. One would now require dC/dt to be given by:

$$-dC/dt = v\left[\int g(x)\,dx;\,x^*\right] \quad (25)$$

and of course Eq. 24 fulfills this requirement only if the $v[\,]$ operator is linear in $g(x)$.

It is important to realize that the conclusion that the SCI requirement can be satisfied only for linear kinetics is a consequence of the assumption of independent kinetics. That is why such an assumption is indeed very restrictive, and it leads to the difficulties of a continuous description that were pointed out by Luss and Hutchinson (1971). If the assumption of independent kinetics is relaxed, the SCI requirement can in fact always be satisfied by a proper formulation of the lumping procedure, and indeed one is faced with the opposite problem: that one could write the kinetic equation in the mixture in infinitely many different ways, all of which would satisfy the SCI requirement.

Lumping of Generalized LIK Mixtures

Consider again the LIK case described by Eq. 8. In a mixture where many components can undergo that type of reaction, the kinetic equation for the Ith component would be:

$$-dc_I/dt = k_I c_I/(1 + \Sigma K_I c_I) \quad (26)$$

since all reactants would compete for the same sites on the catalyst. Several important aspects of Eq. 26 should be noted:

1. The kinetics are not independent, since the rate of the Ith reaction depends on the concentration of all reactants.
2. The rate of reaction of component I is given by the product of a term that is linear in the concentration of reactant I and a term that depends on the concentration of all reactants.
3. All parameters appearing on the righthand side of Eq. 26 can be determined with experiments on single reactants; i.e., the mixture behavior is completely determined by the values of the $\boldsymbol{P}$ vectors. (This provides evidence that the fact that the kinetics are determined by the $\boldsymbol{P}$ values does not imply that they are independent.)
4. The factor $1/(1 + \Sigma K_I c_I)$, which makes the righthand side globally nonlinear, is the same for all reactants.

As will be seen in the following, properties 1 and 2 are of a rather general nature, and the procedure for lumping nonlinear kinetics can be developed on this basis. Not all nonlinear kinetics enjoy properties 3 and 4; we will use the term "generalized LIK mixtures," GLIKM, for those mixtures that enjoy property 3, and the term "uniform generalized LIK mixtures," UGLIKM, for those that enjoy property 4 as well. In this section, we limit attention only to GLIKM, and we discuss the nonlinear lumping procedure for them.

However, before doing so it is of interest to observe that Eq. 26 describes a set of irreversible reactions, so that the equilibrium condition is simply that all concentrations are zero. In a neighborhood of equilibrium, the denominator of the righthand side of Eq. 26 becomes unity, and thus k_I is recognized as the pseudofirst-order kinetic constant near equilibrium. Although this conclusion may seem trivial at this stage, its importance will appear in the discussion of thermodynamics to be given in the last section of this paper.

We begin by observing that in the case of a single component, Eq. 1 could be written in general in the following form:

$$-dc/dt = kcR[Kc;\,\boldsymbol{\beta}] \quad (27)$$

where $R[\,]$ is a function of Kc that also depends parametrically on $\boldsymbol{\beta}$. The value of $R[\,]$ is dimensionless and so is the operator $R[\,]$ itself. In the linear case $R[\,]$ has a constant value of unity. When $R[\,]$ is not independent of its first argument, the kinetics are nonlinear and the value of $R[\,]$ can be called a nonlinearity factor. If the reaction is irreversible, $R[\,]$ can be normalized so that $R[0;\boldsymbol{\beta}] = 1$, which identifies the value of k as the pseudofirst-order kinetic constant in the neighborhood of the equilibrium point $c = 0$. This is the appropriate normalization in the case of mixtures in which irreversible reactions take place, since in such mixtures the concentrations of individual species may well be vanishingly small even if the total concentration is significantly different from zero.

When writing the corresponding equation for that same component in a mixture, one cannot substitute gdx for c everywhere, since the dx would not cancel out except in the linear case where $R[\,]$ is independent of its second argument. However, if one substitutes gdx for c on the lefthand side and in the factor c on the righthand side, the dx does cancel out, and the remaining question is how should one write the nonlinearity factor for the generic component of a mixture?

There are two constraints to be imposed. First, the nonlinearity factor should be such that it degenerates into $R[Kc;\,\boldsymbol{\beta}]$ in the single-reactant case. Second, its expression should not contain dx. Equation 26 suggests the general way of doing this: the nonlinearity factor depends on the weighed concentrations of all reactants in the mixture, and hence, in the continuous description, it has to be expressible as a functional of the weighed concentration distribution function $K(x)g(x, t)$. Thus we write the kinetic equation for the generic species in a continuous GLIKM as follows:

$$-\partial g(x, t)/\partial t = k(x)g(x, t)f\{K(x)g(x, t); x\} \tag{28}$$

where $f\{\,\}$ is a functional of the weighed distribution function, which also depends parametrically on the label x. Functionals that depend parametrically on some parameter arise naturally in the thermodynamic theory of continuous reacting mixtures (Aris and Gavalas, 1966), and in the thermodynamic theory of viscoelasticity (Astarita, 1975). The crucial point to be noted about Eq. 28 is the dimensional aspect of it. Provided that $k(x)$ can be identified properly (a point discussed in detail in the last section of this paper), both the function argument of $f\{\,\}$, $K(x)g(x, t)$, and the parameter argument x are dimensionless, and so is the value; it follows that the operator $f\{\,\}$ itself is dimensionless. This makes Eq. 28 in some sense a quasilinear kinetic equation: the rate $\partial g/\partial t$ is proportional to g itself, the proportionality factor being an intrinsic frequency factor $k(x)$ times a dimensionless number that depends on a dimensionless concentration distribution and a dimensionless label.

Now in the case where there is only one reactant present, characterized by some value $P(x^*)$ of the kinetic vector, the distribution function is proportional to a Dirac delta function:

$$K(x)g(x, t) = K(x^*)c(t)\delta(x - x^*) \tag{29}$$

Since the distribution function in Eq. 29 is entirely determined by the values of c and x^*, the value of the functional $f\{\,\}$ depends only on $K(x^*)c$ and $\beta(x^*)$. It reduces properly to the nonlinearity factor for the single-component case provided that:

$$f\{K(x^*)c\delta(x - x^*); x^*\} = R[K(x^*)c; \beta(x^*)] \tag{30}$$

The SCI requirement is also guaranteed to be satisfied. In fact, the rate of change of the total concentration is given by:

$$\begin{aligned} dC/dt &= \int (\partial g/\partial t)\, dx \\ &= -\int k(x)g(x, t)f\{K(x)g(x, t); x\}\, dx \end{aligned} \tag{31}$$

and if $g(\,)$ is:

$$g(x, t) = C(t)\delta(x - x^*) \tag{32}$$

one obtains:

$$\begin{aligned} -dC/dt &= k(x^*)Cf\{K(x^*)C\delta(x - x^*); x^*\} \\ &= k(x^*)CR[K(x^*)C; \beta(x^*)] \end{aligned} \tag{33}$$

as required. Notice however that the constraint in Eq. 30 does not determine the functional $f\{\,\}$: different functionals may satisfy the SCI requirement.

The LIK described by Eq. 26 are a special case of Eq. 27. Indeed, for LIK the functional $f\{\,\}$ is given by:

$$f\{K(x)g(x, t); x\} = [1 + \int K(x)g(x)\, dx]^{-1} \tag{34}$$

Notice that although the righthand side of Eq. 34 is of a particularly simple form, it still defines a nonlinear functional. Equation 34 is special in that the righthand side does not depend on x explicitly, since there is no β vector to worry about; the mixture considered is a UGLIKM.

Sketch of Solution Techniques

The purpose of this paper is not to provide the solution to any given nonlinear lumping problem, but only to present some basic ideas on the general mathematical structure of such problems. Although attention has been restricted to a comparatively simple case, the governing equations have been shown to be functional-differential ones, and their solution undoubtedly implies significant mathematical difficulties. However, a formal solution can be found for the case of UGLIKM, and this is sketched below.

For an UGLIKM, $f\{\,\}$ does not depend parametrically on x, and therefore:

$$-\partial g(x, t)/\partial t = k(x)g(x, t)f\{K(x)g(x, t)\} \tag{35}$$

Let a 0 subscript identify one particular reference component. Equation 35 implies that:

$$d \ln g(x, t)/d \ln g(x_0, t) = k(x)/k(x_0) \tag{36}$$

which integrates to:

$$\begin{aligned} &[1/k(x)] \ln [g(x, t)/g(x, 0)] \\ &\qquad = [1/k(x_0)] \ln [g(x_0, t)/g(x_0, 0)] = -u(t) \end{aligned} \tag{37}$$

Thus:

$$g(x, t) = g(x, 0) \exp [-k(x)u(t)] \tag{38}$$

$$C(t) = \int g(x, 0) \exp [-k(x)u(t)]\, dx \tag{39}$$

i.e., the total concentration at time t in an UGLIKM is a linear transform of the initial distribution; in fact it is a Laplace transform, only that the warped time u, rather than time t itself, appears as the transform parameter.

Substitution of Eq. 38 into Eq. 35 yields:

$$du/dt = f\{K(x)g(x, 0) \exp [-k(x)u(t)]\} \tag{40}$$

which is an ordinary differential equation for $u(t)$, subject to the initial condition $u(0) = 0$. This can always be solved numerically once the mathematical form of the $f\{\,\}$ functional and the initial distribution $g(x, 0)$ have been assigned.

Once $u(t)$ has been obtained by integration of Eq. 40, the rates of change of the individual species concentration and of the total concentration are immediately obtained as:

$$\begin{aligned} -\partial g/\partial t &= k(x)g(x, 0) \exp [-k(x)u(t)] \\ &\quad \cdot f\{g(x, 0) \exp [-k(x)u(t)]\} \end{aligned} \tag{41}$$

$$-dC/dt = f\{g(x,\ 0)\exp[-k(x)u(t)]\} \cdot \int k(x)g(x,0)\exp[-k(x)u(t)]\,dx \quad (42)$$

In particular, consider the LIK case described by Eq. 26, where $f\{\ \}$ is given by Eq. 34. Let the initial concentration distribution be given by:

$$X^a\Gamma(a)g(x,0) = C(0)x^{a-1}\exp(-x/X) \quad (43)$$

with $a > 0$; X is the average value of x, and $\Gamma(\ )$ is the gamma function. Furthermore, let:

$$k(x) = k^*x/aX; \quad \Gamma(a+\gamma)K(x) = \Gamma(a)K^*(x/X)^\gamma \quad (44)$$

where $a + \gamma > 0$, and k^* and K^* are the average values of k and K. The parameter a assigns the shape of the initial distribution, with $a = 1$ corresponding to an exponential distribution, and $a = \infty$ corresponding to a delta function (single component). Define:

$$x = Xx'; \quad t' = k^*t; \quad k(x)u(t) = x'u'(t); \quad Q = K^*C(0) \quad (45)$$

One now obtains, after some algebra:

$$C(t)/C(0) = W(t) = [1 + u'(t)]^{-a} \quad (46)$$

$$\int K(x)g(x,t)\,dx = QW^{\Omega}, \qquad \Omega = 1 + \gamma/a \quad (47)$$

$$adu'/dt = [1 + W^{\Omega}]^{-1} \quad (48)$$

However, one does not in fact need to integrate Eq. 48, since:

$$-dW/dt = W^{(a+1)/a}/(1 + QW^{\Omega}) \quad (49)$$

As a approaches ∞ (single component) this reduces to $-dW/dt = W/(1 + QW)$ as required. For $a = 1$, it reduces to $-dW/dt = W^2/(1 + QW^{1+\gamma})$; i.e., second-order behavior is predicted at sufficiently large times. (We are indebted to Aris for a personal communication, 1987, suggesting the analysis following Eq. 42.)

It is perhaps clear that a similar procedure will produce a solution for any UGLIKM. However, the procedure makes crucial use of the fact that the functional is uniform—i.e., that it does not depend parametrically on x—and thus it cannot be generalized.

Functional Expansion for GLIKM

A simple way of writing a functional that is guaranteed to satisfy the SCI requirement for a GLIKM is as follows:

$$f\{K(x)g(x,t);x\} = R\left[\int K(x)g(x,t)\,dx;\beta(x)\right] \quad (50)$$

However, Eq. 50 implies the assumption that $f\{\ \}$ depends parametrically on x only through the value of $\beta(x)$; i.e., that the β values for other components do not influence the kinetics of any given reactant. That of course does not need to always be the case, as the following analysis shows.

Functionals may often be expanded in series of integrals (Riesz and Nagy, 1955). A possible expansion is:

$$f\{K(x)g(x);x\} = 1 + \int u_1(x)K(x)g(x)\,dx + \int\int u_2(x,y)K(x)g(x)K(y)g(y)\,dx\,dy + \ldots \quad (51)$$

The kernels $u_N(\ )$ now guarantee that components other than the one considered may influence its kinetics through their own value of β.

The SCI requirement can now be used to infer information on the kernels. Suppose that $R[\ ]$ for the single-component case can be Taylor-series expanded around $Kc = 0$:

$$R[0;\beta] = 1 + \{\partial R[0;\beta]/\partial(Kc)\}Kc + \{\partial^2 R[0;\beta]/\partial(Kc)^2\}K^2c^2/2 + \ldots \quad (52)$$

When the distribution function is that in Eq. 32 the expansion in Eq. 51 yields:

$$f\{K(x^*)c\delta(x - x^*);x^*\} = 1 + u_1(x^*)K(x^*)c + u_2(x^*,x^*)K(x^*)^2c^2 + \ldots \quad (53)$$

The first kernel is entirely determined by the SCI requirement, since the following equation:

$$u_1(x^*) = \partial R[0;\beta(x^*)]/\partial(Kc) \quad (54)$$

must hold for arbitrary values of x^*. However, higher order kernels are not entirely determined, since, for example, the second-order kernel is only subject to the following condition, which needs to hold for arbitrary values of x^*:

$$2u_2(x^*,x^*) = \partial^2 R[0;\beta(x^*)]/\partial(Kc)^2 \quad (55)$$

and its values when the two arguments are not equal to each other are left unspecified by the SCI requirement. The reason for this is of course that different functionals may satisfy the SCI requirement. An understanding of the chemistry of interactions between different components is needed in order to write down the appropriate functional for any given GLIKM.

This conclusion is best understood by considering again Eq. 26. It is true that all the parameters appearing in it can be measured with single-reactant experiments; however, there would be nothing intrinsically impossible, for example, in the following kinetic equation for a discrete mixture, which also contains only parameters measurable in single-reactant experiments, and which also properly degenerates in the case of a single reactant:

$$-dc_I/dt = K_Ic_I/[1 + K_Ic_I(\Sigma K_Jc_J + 1)] \quad (56)$$

where the sum is intended over J different from I. It is our understanding of the chemistry which leads to writing the equation in the form of Eq. 26 and not of Eq. 56; it is not experimental information obtained with single-component systems. However, if enough understanding of the chemistry involved is available to write down with confidence the kinetic equation for a discrete mixture, extension to the continuous case should be straightforward.

Formally, it is possible to define a subclass of GLIKM, called SCI-GLIKM, as those GLIKM for which the SCI requirement entirely determines the kinetic functional. Thus for a SCI-GLIKM all higher order kernels have zero values unless all the arguments are equal to each other. With this assumption, some tedious algebra shows that the expansion in Eq. 51 results in Eq. 50, i.e., an explicit analytical form for the functional has been obtained.

It is of interest to observe that Eq. 26 is one where the discrete description of the mixture is simply obtained by substituting $\Sigma K_J c_J$ for Kc in the $R[\ ]$ operator determined by the single-component experiments. It is therefore not surprising that in the continuous description, one can simply substitute for Kc the integral of the weighed distribution function of concentrations.

Bimolecular Systems

We now turn attention to the generalization of the DR case. Equation 9 is dimensionally peculiar, as discussed earlier, and in contrast to the GLIKM case, there is no obvious way of identifying the normalizing factor K. Of course, Eq. 9 can be reduced to the form of Eq. 27 by writing:

$$-dc/dt = kKc^2 \tag{57}$$

but there are infinitely many ways of decomposing b into the product kK. This, however, turns out to be an artifact arising from the singularity of the limit of irreversible reactions, and both k and K are indeed identifiable when one accounts for reversibility. This point is clarified in the last section of this paper.

Now in a mixture of N components which may undergo bimolecular reactions one would have, if the products cannot themselves react consecutively:

$$-dc_I/dt = c_I \Sigma k_{IJ} c_J \tag{58}$$

where the k_{IJ}'s are bimolecular kinetic constants. This is in essence the case considered by Li (1984). The matrix k_{IJ} is symmetrical. The mixture is obviously not a GLIKM, since the off-diagonal elements of the k_{IJ} matrix cannot be determined by single-component experiments. They can, however, be determined by experiments made with only two reactants present, and this suggests a generalized definition of bimolecular systems (BS): a BS is a mixture whose kinetic behavior is entirely determined by parameters the values of which can all be determined by experiments with no more than two reactants present.

The description in Eq. 58 is based on mass action kinetics, and the purpose here is both to generalize Eq. 58 to the continuous case, and to generalize the problem by allowing for kinetics other than the mass action one. Extension of the mass action case to the continuous description is comparatively trivial. However, it is useful to consider this special case after some preliminary analysis of the more general case.

Components other than I appear in Eq. 58 through a weighed sum of their concentrations, but the terms in the sum are not dimensionless. They can be made dimensionless by rewriting Eq. 58 in the following form:

$$-dc_I/dt = k_I c_I \Sigma K_{IJ} c_J \tag{59}$$

where:

$$K_{IJ} = k_{IJ}/k_I \tag{60}$$

and k_I has dimensions of a frequency.

Three important observations are in order concerning Eq. 60. First, while k_{IJ} is symmetric, K_{IJ} need not be symmetric. Second, the normalizing factor for component J, K_{IJ}, depends on which particular component I is being considered, in contrast to the GLIKM case. Finally, there are of course infinitely many ways of effecting the decomposition in Eq. 60, but this is again an artifact arising from the singularity of the irreversible limit.

Now suppose the kinetics are not of the mass action type, but the system is still a BS. Thus all parameters of interest can be obtained with two-reactant experiments, the result of which will in general be expressible as follows:

$$-dc_I/dt = k_I c_I R_I[K_{II} c_I, K_{IJ} c_J] \tag{61}$$

where the subscript I of the dimensionless $R_I[\ ]$ operator reminds us that a different operator may apply for each reactant.

We now turn attention to the continuous description of a non-mass-action kinetics bimolecular system. Let x be the label of the reactant one is considering, and y the label of the reactant with which interactions are considered (x corresponds to I and y to J). Correspondingly, the frequency factor will be $k(x)$, and the interaction parameter will be $K(x, y)$. The kinetics in the continuous description will be given by:

$$-\partial g(x)/\partial t = k(x)g(x)F\{K(x, y)g(y); x\} \tag{62}$$

where $F\{\ \}$ is a functional of the weighed distribution function $K(x, y)g(y)$ which also depends parametrically on x, just as $R_I[\ ]$ depends on I.

The functional $F\{\ \}$ is now subject, in addition to the SCI requirement, to a two-components identity (TCI) requirement; in actual fact, the former is a special case of the latter. The TCI requirement is that the functional $F\{\ \}$ must degenerate to the nonlinearity factor $R_I[\ ]$ in Eq. 61 when the distribution function is given by:

$$g(y) = c_I\delta(y - y_I) + c_J\delta(y - y_J) \tag{63}$$

The single-component identity is simply read off as the special case of the TCI where $c_J = 0$.

In the special case of mass action kinetics (where Eq. 59 holds in the discrete description), the continuous description is:

$$-\partial g(x)/\partial t = k(x)g(x) \int K(x, y)g(y)\, dy \tag{64}$$

i.e., the functional $F\{\ \}$ is linear, and the equation is obtained by simply substituting the integral of the weighted distribution function for the sum appearing in the discrete description (in analogy with the case discussed in the previous section). The fact that the functional appearing on the righthand side is linear is the reason why the linear matrix analysis of Li (1984) is possible for this case.

The functional in Eq. 64 quite obviously satisfies the TCI requirement. In particular, should there be only one component in the mixture, say the concentration distribution function is as in Eq. 32, Eq. 64 reduces to Eq. 9 with $b = k(x^*)K(x^*, x^*)$, as required.

The rate of change of the total concentration is given by:

$$-dC/dt = \int \int K(x, y)k(x)g(x)g(y)\, dx\, dy \tag{65}$$

which, when $g(\ )$ is given by Eq. 63, reduces to:

$$-dC/dt = k(x_I)[K(x_I, x_I)c_I + K(x_I, x_J)c_J]c_I + k(x_J)[K(x_J, x_I)c_I + K(x_J, x_J)c_J]c_J \quad (66)$$

as required.

Although a formal solution has not been given, it is evident that the overall apparent order of reaction will turn out to be larger than two. In fact, species with large frequency factors will disappear more quickly at the beginning, and hence the "average" value of the frequency factor will decrease as time progresses; since at any given value of the average frequency factor the overall kinetics would be second order, the apparent overall kinetics will appear of order larger than two. This is the somewhat obvious extension of the classical Aris (1968) result that the apparent overall order of reaction in the case of linear kinetics is larger than one.

The conclusion in the preceding paragraph is based on a heuristic argument, but it can be put on a firmer basis by considering a special case. Suppose that, in the discrete description, the kinetic constant k_{IJ} can be expressed as $k_I K_J$. This is a very restrictive condition, of course, since now the matrix is not only to be symmetric, but all its rows are proportional to each other, and so are all its columns. However, this makes the continuous representation a uniform one, since $K(y)$, rather than $K(x, y)$, appears as the kernel of the integral in Eq. 64. With this, an explicit solution can be found:

$$g(x, t) = g(x, 0) \exp[-k(x)u(t)] \quad (67)$$

$$C(t) = \int g(x, 0) \exp[-k(x)u(t)]\, dx \quad (68)$$

where $u(t)$ is the solution of the following differential equation:

$$du/dt = \int K(y)g(y, 0) \exp[-k(y)u(t)]dy; \quad u(0) = 0 \quad (69)$$

In the special case where the initial concentration distribution is exponential:

$$Xg(x, 0) = \exp(-x/X) \quad (70)$$

and

$$k(x) = k^*x/X; \quad K(x) = K^*x/X \quad (71)$$

Equation 69 integrates to:

$$u + k^*u^2 + k^{*2}u^3/3 = K^*C(0)t; \quad u \geq 0 \quad (72)$$

and one obtains:

$$C(t) = C(0)/(1 + k^*u) \quad (73)$$

It may be seen, by eliminating u and t between Eqs. 65, 72, and 73, that $C(t)$ behaves as if of the fourth order. In general, by choosing $g(x, 0)$ and $K(x)$ appropriately, the apparent kinetics can be of any order greater than two (Aris, 1987).

Now consider the possibility of expanding the functional $F\{\ \}$ in a series of integrals, say:

$$F\{K(x, y)g(x); x\} = 1 + \int u_1(x{:}y)K(x, y)g(y)\, dy + \int\int u_2(x; y, z)K(x, y)g(y)k(x, z)g(z)\, dy\, dz + \ldots \quad (74)$$

The dependence of the kernels $u_N(\ )$ on x (before the semicolon) reflects the parametric dependence of the functional on x; the variables after the semicolon are dummy integration variables. Taking the value of unity for the first term in the expansion is the required normalization for irreversible reactions, in that it sets $k(x)$ at the pseudofirst-order kinetic constant in the neighborhood of the equilibrium composition (see the last section for a detailed discussion of this point).

With the same normalization, the operator $R_I[\ ]$ may be series expanded as follows:

$$\begin{aligned} R_I[K_{IJ}c_I, K_{IJ}c_J] &= R_x[x, y] \\ &= 1 + (\partial R_x[0, 0]/\partial x)x \\ &\quad + (\partial R_x[0, 0]/\partial y)y \\ &\quad + (\partial^2 R_x[0, 0]/\partial x^2)x^2/2 \\ &\quad + (\partial^2 R_x[0, 0]/\partial y^2)y^2/2 \\ &\quad + (\partial^2 R_x[0, 0]/\partial x\partial y)xy + \ldots \end{aligned} \quad (75)$$

The TCI requirement imposes restrictions on the kernels of the integral expansion:

$$u_1(x; x) = \partial R_x[0, 0]/\partial x \quad (76)$$

$$u_1(x; y) = \partial R_x[0, 0]/\partial y \quad (77)$$

$$u_2(x; x, x) = (\partial^2 R_x[0, 0]/\partial x^2)/2 \quad (78)$$

$$u_2(x; y, y) = (\partial^2 R_x[0, 0]/\partial x^2)/2 \quad (79)$$

$$u_2(x; x, y) + u_2(x; y, x) = \partial^2 R_x[0, 0]/\partial x\partial y \quad (80)$$

which need to hold for arbitrary choices of the labels x and y. Equations 76 and 77 determine completely the first-order kernel; eqs. 78 and 79 determine the second-order kernel when the values of the two variables following the semicolon are equal to each other. Even with the (unwarranted) assumption that the second-order kernel is symmetrical with respect to the two variables following the semicolon, Eq. 80 determines it only when one of the two variables has the same value as the label preceding the semicolon. Even weaker constraints are imposed by the TCI requirement for the kernels of order higher than two; for instance, the third-order kernel's values are determined only when at least two of the variables following the semicolon are equal to each other, and at least one of them is equal to the label preceding it.

It is, of course, again possible to define a restricted class of bimolecular systems, TCI-BS, as systems where the functional is entirely determined by the TCI requirement. This would imply that for a TCI-BS those values of the kernels which cannot be determined from the TCI requirement are zero. Even more tedious algebra is needed to show that this would correspond to writing the functional in the following form:

$$F\{K(x,y)g(y);x\} = R_x[K(x,x)g(x), \int K(x,y)g(y)\,dy] \quad (81)$$

i.e., again an explicit analytical form has been obtained. This is likely to be correct if, in the discrete description, the influence of components other than I only appears through a sum of appropriately weighted concentrations, as indeed is the case for mass action kinetics.

Thermodynamics

All reactions considered so far are irreversible. The statement that a reduction is irreversible is a thermodynamic one. The continuous thermodynamics of mixtures was proposed in 1931 by DeDonder, and a discussion is given by Aris and Gavalas (1966) and by Astarita (1988). Only the very fundamental elements of it are discussed below, in order to set the stage for the appropriate normalization and functional expansion for reversible reactions. In the development below, we combine the continuous description methodology of Aris and Gavalas (1966) with the type of second law analysis used by Truesdell (1984) in his dicrete description. The main point that we wish to make is: the assumption that kinetics can be linearized near equilibrium, thus yielding a system of maximal rank, is implicit in the usually accepted description of equilibrium itself.

Before considering the thermodynamics of a continuous mixture, it is useful to point out that even in the simple single-reactant case, the situation where the reaction is irreversible is a singular limit of the general case where it is reversible. Indeed, consider for example the case of a reversible dimerization reaction, for which the kinetics would be given by:

$$-dc/dt = b(c^2 - c_2/P) = b(c^2 - c^{*2}) \quad (82)$$

where c_2 is the dimer concentration, P is the concentration-based equilibrium constant, and c^* is the equilibrium concentration of the monomer. Now suppose that the actual monomer concentration is in a neighborhood of the equilibrium value, say:

$$c = c^* + h; \quad h \ll c^* \quad (83)$$

The rate of reaction would be given by:

$$-dc/dt = 2bc^*h + O[(h/c^*)^2] \quad (84)$$

i.e., it would be linear in the displacement from equilibrium h, and not quadratic. The frequency factor k would thus be identified with $2bc^*$ and the normalization factor K with $1/(2c^*)$, which of course are both degenerate in the case of an irreversible reaction. However, real reactions are never truly irreversible, and hence a neighborhood of the equilibrium point where the kinetics are linear in the displacement from equilibrium could well exist also for reactions that are not first order. The assumption that such a neighborhood exists is equivalent to the assumption that the kinetic equation is invertible at the equilibrium point. As discussed below, such an assumption is in fact a very mild one, and one that is invariably made (albeit implicitly) in the theory of chemical equilibria.

Turning attention now to the continuous description, one notes that since one is dealing with a mixture with a continuum of reactants, a continuum of reactions needs to be considered. Let v be the reaction label, and let $\sigma(v,x)$ be the stoichiometric coefficient of species x in reaction v. The mass conservation constraint implies that:

$$\int \sigma(v,x)m(x)\,dx = 0 \quad \text{for all } v \quad (85)$$

where $m(x)$ is the mass distribution function. In actual fact, the permanence of atoms imposes an even stronger constraint, but that does not serve any useful purpose in the present context.

A finite set of M reactions is independent if the rank of the stoichiometric coefficients matrix is M. This concept can be extended to a continuum of reactions as follows: the continuum of reactions $\sigma(v,x)$ is independent if the following equation for the multipliers $p(v)$:

$$\int p(v)\sigma(v,x)\,dv = 0 \quad (86)$$

has only the trivial solution $p(v) = 0$, i.e., if $\sigma(v,x)$ is orthogonal only to the zero function for all x. This guarantees that extents of reaction $q(v)$ are uniquely determined by the following equation:

$$dm(x) = \int \sigma(v,x)\,dq(v)\,dv \quad (87)$$

Now at fixed temperature and pressure the free enthalpy (often called the Gibbs free energy) depends solely on composition, say:

$$G = G\{n(x)\} \quad (88)$$

where $n(x)$ is the number of moles distribution function, $n(x) = m(x)/M(x)$ if $M(x)$ is the molecular weight of component x. Given an initial composition $n_0(x)$, Eq. 87 determines $n(x)$ at any later time in terms of $q(v)$: the $n(x)$ distribution is restricted to the reaction subspace determined by the $q(v)$ distribution through Eq. 87.

Since free enthalpy is an absolutely additive function of mass, the following equation holds true:

$$G\{\alpha n(x)\} = \alpha G\{n(x)\} \quad (89)$$

If $G\{n(x)\}$ is subtracted from both sides of Eq. 89, the result is expressed in terms of the expansion of $G\{\,\}$ in Frechet differentials truncated at the second term, and if the limit for α approaching unity is taken, one obtains:

$$G\{n(x)\} = \int G'\{n(x);x\}n(x)\,dx \quad (90)$$

where $G'\{\,\}$ is the functional derivative of $G\{\,\}$, i.e., the kernel of the integral representation of its first Frechet differential. Equation 90 allows us to interpret the functional derivative of $G\{\,\}$ as the chemical potential $\mu(x)$, say:

$$G = \int \mu(x)n(x)\,dx \quad (91)$$

which is obviously the analog of the classical equation holding in the discrete description.

It is now possible to represent the affinity of all reactions, $\theta(v)$, as:

$$\theta(v) = dG/dq(v) = \int \sigma(v, x)\mu(x)\, dx \tag{92}$$

Now let $r(v) = dq(v)/dt$ be the rate of the v reaction. Algebraic rearrangement of the equations above yields:

$$dG/dt = \int \theta(v)r(v)\, dv \tag{93}$$

and the second law of course requires dG/dt to be nonpositive. Actually, the usual assumption in chemistry (Shinnar and Feng, 1985) is a stronger one, since it amounts to requiring that the integrand in Eq. 93 be identically nonpositive. Without need for this stronger assumption, one only needs to consider that when the system is at equilibrium, $r(v) = 0$, and thus the righthand side of Eq. 93 has a maximum at the equilibrium composition of the mixture $n^*(x)$, to obtain the results below.

Since Eq. 87 determines $n(x)$ in terms of $q(v)$, all constitutive equations can be written as functionals of the extent of reactions distribution function, which also depend parametrically on the label v of the particular reaction considered, say, for example, for the reaction rate distribution and for the affinity distribution:

$$r(v) = \mathbf{R}\{q(w); v\} \tag{94}$$

$$\theta(v) = \boldsymbol{\Theta}\{q(w); v\} \tag{95}$$

Since the righthand side of Eq. 93 has a maximum at $q(w) = q^*(w)$, its first Frechet differential is zero at the equilibrium point. Since at equilibrium $r(v) = 0$, this reduces to the requirement that the following equation is satisfied for an arbitrary function $s(w)$ measuring displacement from equilibrium:

$$\int\int \boldsymbol{\Theta}\{q^*(w); v\}u^*(w; v)s(w)\, dv\, dw = 0 \tag{96}$$

where $u^*(w; v)$ is the functional derivative of $\mathbf{R}\{q(w); v\}$ at $q(w) = q^*(w)$, which of course also depends parametrically on v.

Now let $\mathbf{D}$ be the set of functions $f(w)$ to which the functional derivative $u^*(w; v)$ is orthogonal, i.e., functions for which:

$$\int u^*(w; v) f(w)\, dw = 0 \tag{97}$$

Of course, the transpose of the functional derivative $u^*(v; w)$ is orthogonal to all $f(v)$ in $\mathbf{D}$. Given any displacement from equilibrium $\epsilon s(w)$ resulting in some reaction rates $\epsilon r(v)$ given by:

$$r(v) = \int u^*(w; v)s(w)\, dw \tag{98}$$

the displacement $\epsilon[s(w) + f(w)]$ would result in the same rates $\epsilon r(v)$, i.e., $\mathbf{R}\{q^*(w); v\}$ would not be invertible. Correspondingly, the equilibrium affinity would be:

$$\theta^*(v) = \boldsymbol{\Theta}\{q^*(w); v\} = f(v) \tag{99}$$

However, if $\mathbf{R}\{q(w); v\}$ is invertible at $q(w) = q^*(w)$, $\mathbf{D}$ contains only the zero function $0(w)$, and hence Eq. 99 reduces to the requirement that the affinity at equilibrium is identically zero:

$$\theta^*(v) = 0 \tag{100}$$

or, equivalently:

$$\int \sigma(v, x)\mu^*(x)\, dx = 0 \quad \text{for all } v \tag{101}$$

Equation 101 determines (in principle) the equilibrium composition $n^*(x)$.

Truesdell (1984) defines as a strong equilibrium one where the discrete description equivalent of Eq. 100 holds, thus distinguishing it from weak equilibria that might occur should $u^*(w;v)$ be orthogonal to some nonzero function. However, since the discrete description equivalent of Eq. 101 is invariably regarded as appropriate in the theory of chemical equilibria, restriction to strong equilibria does not seem to be more than a very mild assumption.

Once the equilibrium composition has been established, and hence the equilibrium concentration distribution function $g^*(x)$, it is an easy matter to define a displacement from equilibrium distribution function $h(x,t)$ as follows:

$$h(x,t) = g(x,t) - g^*(x) \tag{102}$$

and then expand the kinetic functionals in a series of integrals of $K(x)h(x,t)$. With the first term set at unity, $k(x)$ is then appropriately normalized for arbitrary reversible reactions. This of course implies that pseudofirst-order behavior with respect to displacement from equilibrium holds in a neighborhood of equilibrium, but this is nothing else but the assumption of invertibility of $\mathbf{R}\{q^*(w);v\}$ that restricts equilibria to only strong ones. In other words, one is faced with only two possibilities: either one wants to regard Eq. 101 as the appropriate description of equilibrium (which is universally the case), and then it follows that linearization of kinetics near equilibrium is not an independent assumption; or one wants to regard the latter as an independent assumption, but then if such is the case one is at a loss about the appropriate description of equilibrium.

Turning attention back to the normalization of kinetics, consider the case where there is only one reaction in the mixture, sav $v = V$, and hence only one extent of reaction:

$$q(v) = q\delta(v - V) \tag{103}$$

Now Eq. 98 would reduce to:

$$r(V) = u^*(V;V)s(V) \tag{104}$$

and $u^*(V; V)$ is different from zero by the assumption of invertibility. $u^*(V; V)$ has units of a frequency, and can thus be taken as the intrinsic pseudofirst-order kinetic constant of the reaction. The kinetic constant for species x can thus be chosen as:

$$k(x) = \int \sigma(v,x)u^*(v;v)\, dv \tag{105}$$

which provides the required normalization for all species in the mixture.

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Notation

a = parameter, Eq. 43
b = kinetic n-order constant

c = concentration of single reactant
c' = dimensionless concentration
c_I = concentration of species I
$\mathbf{c}$ = vector of concentrations
C = total concentration of reactants
c^* = equilibrium concentration of monomer
c_2 = concentration of dimer
D = set of $f(\ )$ functions
$f(\ )$ = functions to which $u^*(\ )$ is orthogonal
f = kinetic functional for GLIKM
F = kinetic functional for BS
$F[\ ]$ = function, Eq. 13
$g(\ )$ = concentration distribution
$g^*(\ )$ = equilibrium concentration distribution
G = free enthalpy
$G\{\ \}$ = constitutive functional for G
$G'\{\ \}$ = functional derivative of $G\{\ \}$
h = concentration displacement from equilibrium
$h(\ )$ = displacement from equilibrium concentration distribution
I = label in discrete description
J = dummy label in discrete description
k = frequency factor
$k(\ )$ = frequency factor distribution
k^* = average value of k
k_I = frequency factor for species I
k_{IJ} = bimolecular kinetic constant
K = normalizing factor for concentration
$K(\ )$ = normalizing factor distribution
K^* = average value of K
K_I = K value for species I
K_{IJ} = interaction normalizing factor
$m(\ )$ = mass distribution
$M(\ )$ = molecular weight distribution
n = order of reaction
$n(\ )$ = number of moles distribution
n_o = initial number of moles distribution
$n^*(\ )$ = equilibrium number of moles distribution
$O(\ )$ = zero function
$p(\ )$ = multipliers for independence condition
P = equilibrium constant for dimerization reaction
$\mathbf{P}$ = kinetic parameter vector
$q(\ )$ = extent of reaction distribution
$q^*(\ )$ = equilibrium extent of reaction distribution
Q = dimensionless average value of K
$r(\ )$ = single-reactant kinetic function
$r'(\ )$ = dimensionless form of $r(\ )$
$r_I(\ )$ = $r(\ )$ function for species I
$R[\ ]$ = nonlinearity factor, Eq. 27
$r(v)$ = rate of reaction distribution
$R[\ ]$ = GLIKM single-component nonlinearity factor
$R_I[\ ]$ = BS two-component nonlinearity factor
$\mathbf{R}\{\ \}$ = constitutive functional for $r(\ )$
$s(\ )$ = displacement from equilibrium distribution
t = time
t' = dimensionless time
$u(\ )$ = warped time, Eq. 37
$u'(\ )$ = dimensionless warped time
$u_N(\ )$ = kernels in integral expansion
$u^*(\ )$ = functional derivative of $\mathbf{R}\{\ \}$ at $q(w) = q^*(w)$
v = label of reaction in continuous description
$v[\ ]$ = function, Eq. 23
w = dummy label of reaction in continuous description
x = label of component in continuous description
x' = normalized label
x^* = label of single reactant
x_o = label of reference component
X = average value of x
y,z = dummy labels of component in continuous description

Greek letters

α = arbitrary scalar
$\boldsymbol{\beta}$ = dimensionless kinetic parameter vector
β_J = dimensionless kinetic parameter
τ = exponent, Eq. 44
$\Gamma(\ )$ = gamma function
$\delta(\ )$ = Dirac delta function
$\theta(\ )$ = affinity distribution
$\boldsymbol{\Theta}\{\ \}$ = constitutive functional for $\theta(\ )$
$\mu(\ )$ = chemical potential distribution
$\mu^*(\ )$ = equilibrium chemical potential distribution
$\sigma(\ )$ = stoichiometric coefficient distribution
Ω = exponent, Eq. 47

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